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PETE WILSON, Governor

MEMORANDUM

TO: Dr. John Sanders, Chief
Environmental Monitoring and Pest Management Branch
Department of Pesticide Regulations

FROM: George Lew, Chief
Engineering and Laboratory Branch

DATE: October 3, 1995

SUBJECT: BROMOXYNIL APPLICATION FINAL REPORT

Attached is the final report, "Ambient Air Monitoring after an Application of Bromoxynil in Imperial County during January 1995."

If you or your staff have questions or need further information, please contact me at 263-1630 or Don Fitzell at 263-2041.

Attachment

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State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

AMBIENT AIR MONITORING AFTER AN APPLICATION OF BROMOXYNIL IN IMPERIAL COUNTY DURING JANUARY 1995

Engineering and Laboratory Branch
Monitoring and Laboratory Division

Test Report No. C87-117A

Report Date: October 3, 1995

APPROVED:

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This report has been reviewed by the staff of the Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Ambient Air Monitoring After an Application of Bromoxynil in Imperial County During January 1995

This report presents the results of ambient air monitoring after a ground application by tractor of bromoxynil (Buctril) at a selected onion field in Imperial County. Samples were collected before, during and for 72 hours after the application. No samples analyzed contained bromoxynil above the detection limit (0.04 ug/sample). This results in a detection level of 0.11 ug/m^3 for a three-and-one-half hour sample.

This monitoring was a follow-up to similar sampling conducted in January, 1992 which found low (0.02 to 2.34 ug/m^3), but measurable levels of bromoxynil. A description of the 1992 application monitoring program is presented in the ARB report titled, "Ambient Air Monitoring in Imperial County for Bromoxynil in January, 1992 after Application to a Wheat Field." At the time of the first study, the samplers were located upwind and downwind based on the prevailing wind direction. On site meteorological data indicated the wind was blowing from a different direction when the highest level (2.34 ug/m^3) was detected. For this reason the second study was conducted with four samplers, one placed on each side of the field. No field conditions were observed to explain the lower levels found in this second study, although a lower application rate (one pint per acre versus 1.3 pints per acre) and a different crop (onions versus wheat) may have affected the levels detected.

Acknowledgments

Kevin Mongar of the Air Resources Board assisted in the monitoring and Jack LaBrue was the Instrument Technician. Alton Metcalf and Gerald Edwards of Stoker Company arranged for a suitable field to monitor. Assistance was also provided by Lynn Baker and Ruth Tomlin of the ARB's Air Quality Measures Branch.

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I. INTRODUCTION

The Air Resources Board (ARB) Engineering and Laboratory Branch (ELB) staff conducted a three-day source impacted ambient monitoring program for an application of bromoxynil (Buctril) to an onion field in Imperial County during January of 1995. This monitoring was performed at the request of the California Department of Pesticide Regulation (DPR). This monitoring occurred from January 19 through January 22, 1995. As required by Food and Agricultural Code Section 14021, this monitoring was conducted to provide DPR with data for the evaluation of the persistence and exposure of airborne pesticides.

The Pesticide Use Report for 1992 indicates bromoxynil is most widely used on wheat (42,882 pounds), oats (21,996 pounds), garlic (14,524 pounds), alfalfa (9,889 pounds), and onions (8,784 pounds).

II. DESCRIPTION

Bromoxynil (molecular weight 276.92 g/mole) is a selective herbicide which is a white, odorless solid with a melting point of 194-195^{0}C. It has a vapor pressure of less than 10^{-15} mm Hg at 20^{0}C. It is only slightly soluble in water (0.13 gm/l), but is soluble in acetone (170 gm/l) and tetrahydrofuran (410 gm/l).

Bromoxynil is not regulated as a restricted use material under Section 6400, Title 3 of the California Code of Regulations, but it is a Category II pesticide and subject to the provisions of the Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65). Peak use of this herbicide occurs in Imperial County during the winter months. The primary crop is wheat.

III. SAMPLING LOCATIONS

An onion field of about 28 acres (FIGURE I) was selected by Gerald Edwards of the Stoker Company and approved by ARB staff for application monitoring. Four samplers were set up (see FIGURE II): one on the eastern perimeter (site E) at a distance of about 11 yards from the field, one about 17 yards from the southern perimeter (site S), one about 20 yards from the northern perimeter (site N) and one

approximately 18 yards from the western side of the field (site W). A meteorological station with a strip chart recorder was set up adjacent to site N to determine wind speed and direction. A second meteorological station equipped with a data logger was also set up. Unfortunately, this unit had not been used before and software problems prevented the collection of any data. Site S took duplicate samples to determine precision of the data. All other sites collected single samples.

The application was by tractor and took about 2 and 1/2 hours. The application began in the northeast corner. The tractor traversed from north to south and from east to west. The small section in the southwest corner (south of the house, see FIGURE II) was treated after the remainder of the field was completed. Bromoxynil was the only product applied to the field at this time. The formulation was Buctril by Rhone-Poulenc which contains 33.4% active ingredient (octanoic acid ester of bromoxynil). The application rate was 1.0 pint dissolved in 40 gallons of water per acre. The work order for this application is in APPENDIX I.

IV. SAMPLING METHODOLOGY

The samples were collected using the apparatus shown in APPENDIX II, Attachment I. Measured quantities of air were pulled through the sample tubes containing XAD-2 resin. The tubes are 8 mm x 110 mm, with 400 mg in the primary section and 200 mg in the secondary (SKC catalog #226-09). Any bromoxynil present in the sampled ambient air is captured by the resin contained in the tubes. Subsequent to sampling, the tubes were stored on ice until delivery to the laboratory and then stored in a freezer until analysis was complete.

Sampling trains designed to operate continuously were set up at the four sampling sites identified in FIGURE II. The sampling schedule outlined in the QA Plan (APPENDIX II, Attachment II) was modified so that the sample tubes did not have to be changed in the middle of the night.

Each sample train consisted of an XAD-2 resin tube with tube cover, Teflon fittings and tubing, rain shield, flow meter with valve, train support, and a 12VDC battery-powered vacuum pump. The tubes were placed approximately 1.5 meters above the ground. Each tube was prepared for use by breaking off each sealed glass end and then immediately inserting the tube into a Teflon fitting. The tubes were oriented in the sampling train according to a small arrow printed on the side of each tube indicating the direction of flow. Covers were placed around the tube to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow through a rotometer adjusted with a metering valve to an indicated reading of 2.0 liters per minute (lpm). A leak check was performed by blocking off the sample inlet. The sampling train would be determined to be leak-free, if the indicated flow dropped to zero. Upon completion of a successful leak check, the indicated flow rate was again set at 2.0 lpm and was recorded (if different from the planned 2.0 lpm) along with date, time, and site location. Calibration prior to use in the field indicated that an average flow rate of 1.8 lpm was actually achieved when the rotometers were set to 2.0 lpm. This average flow rate was used to calculate all sample volumes.

At the end of each sampling period the final indicated flow rate (if different than the set 2.0 lpm), the stop date and time were recorded. The XAD-2 tubes were then removed from the sample train, end caps installed on both ends, and identification labels affixed to each tube. Each tube was then placed in a culture tube with a screw cap and stored with ice in a covered chest while in the field. Samples were stored in a freezer in Sacramento until analysis was completed.

V. ANALYTICAL METHODOLOGY

The XAD-2 resin tubes recovered from each sampler were analyzed by ELB staff. The XAD-2 resin in the primary section of each sample tube was extracted with 3 ml acetone. A 3/4 ml aliquot of the extract was evaporated to dryness then redissolved in 3/4 ml HPLC grade water. A C_{18} column with a methanol/water gradient solvent was used for separation by HPLC. Detection was by UV at 280 nanometers. All samples were analyzed within two weeks of collection. A detailed description of the method is presented in the Analytical S.O.P. (APPENDIX III).

The method of analysis was changed from that used in the previous study (gas chromatography/electron capture detection, following derivatization of the sample to it's methyl ester) when it was determined that comparable sensitivity could be achieved with the simpler HPLC method. This change was not known when the protocol was written so the earlier analytical method was described in the protocol.

VI. RESULTS

The monitoring results are shown in TABLE I. A summary of the on-site meteorological data is presented in TABLE II. A combined summary of the monitoring and meteorological data is presented in TABLE III. The laboratory quality control data is presented in TABLE IV. Additional detailed meteorological data from the California Irrigation Management Information System (CIMIS) station, located in Seeley, is presented in

APPENDIX IV. None of the results presented in this report have been corrected for percentage recovery.

TABLE III is a summary of the data in TABLES I and II. As TABLE I shows, no samples analyzed contained bromoxynil above the detection limit (0.04 ug/sample). This amount corresponds to a detection level of 0.11 ug/m^3 for a three and one-half hour sample.

This monitoring was a follow-up to similar sampling conducted earlier (Ambient Air Monitoring in Imperial County for Bromoxynil in January, 1992, after Application to a Wheat Field, APPENDIX V) which found low (0.02 to 2.34 ug/m^3), but measurable levels of bromoxynil. At the time of the first study, the samplers were located upwind and downwind based on the prevailing wind direction. On site meteorological data indicated the wind was blowing from a different direction when the highest level (2.34 ug/m^3) was detected. For this reason the second study was conducted. No field conditions were observed to explain the lower levels found in this second study, although a lower application rate (one pint per acre versus 1.3 pints per acre) and a different crop (onions versus wheat) may have affected the levels detected.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the Analytical S.O.P., (APPENDIX III).

Most of the procedures outlined in the Quality Assurance Plan (APPENDIX II, Attachment II) were followed. The only exception was a modification of the sampling schedule (see SAMPLING METHODOLOGY). In addition, a flow rate audit, a systems audit and an analytical performance audit were performed by the QMOSB (see APPENDIX VI).

All of the spikes prepared by the laboratory conducting the analysis (TABLE IV, Trip Spikes and Blanks, In-House Laboratory Spikes) resulted in good recovery levels. However, a preliminary set of spikes prepared by the QMOSB (TABLE IV) resulted in low recoveries (-49.3 to -80.8%) indicating a systematic error in standards preparation. The second set of spikes prepared by the QMOSB (TABLE IV) resulted in much better agreement (-6.4 to 32.0%). The complete results of the QMOSB audit are presented in APPENDIX VI.

As noted in the QMOSB audit report, the samples were stored longer than the maximum time period covered by the stability studies. However, the high recovery levels for the field spikes, 96%, indicate the delay in analysis did not adversely effect the validity of the data.

FIGURE I. Bromoxynil Monitoring Area

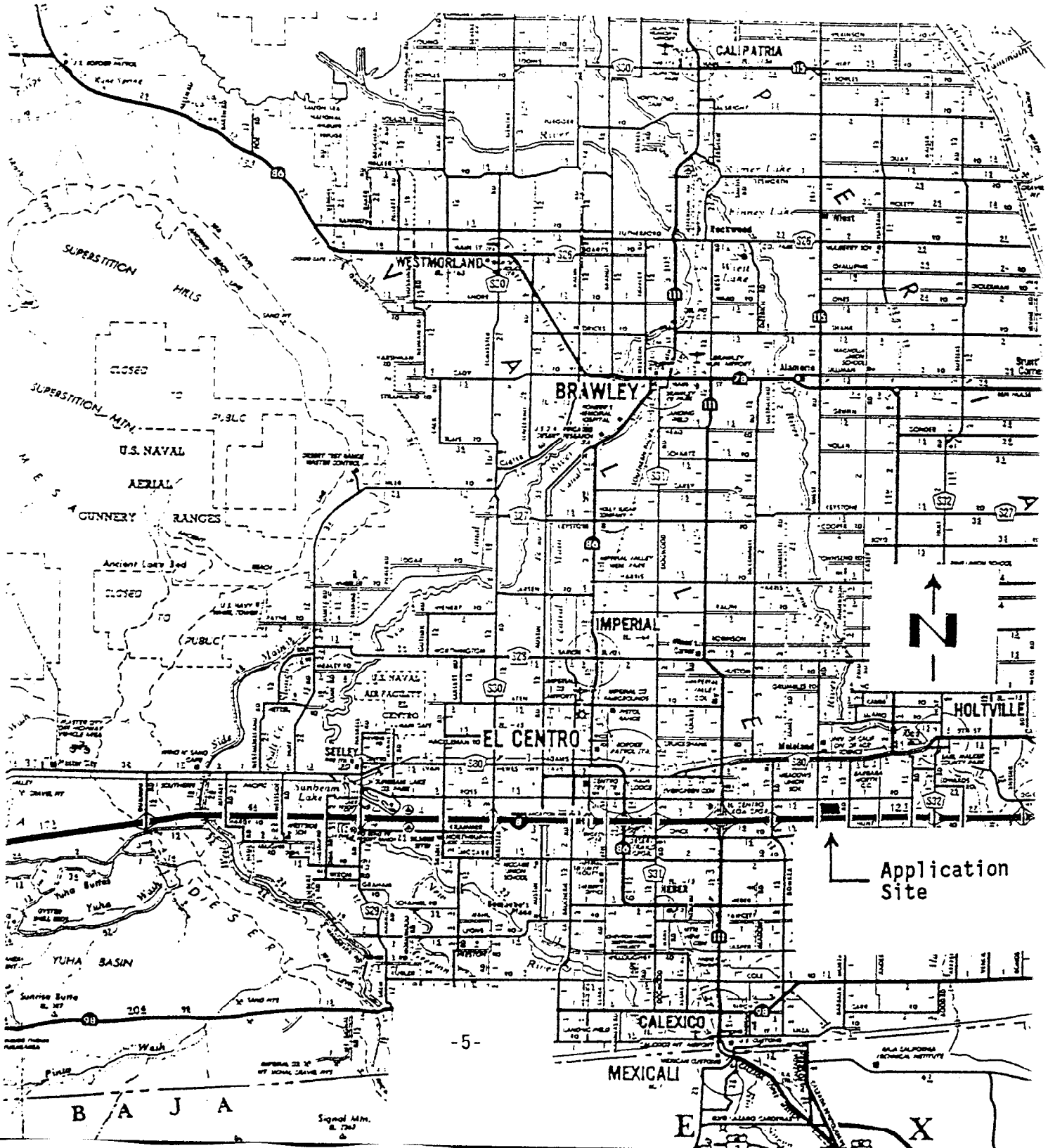


FIGURE II. Bromoxynil Monitoring Sites

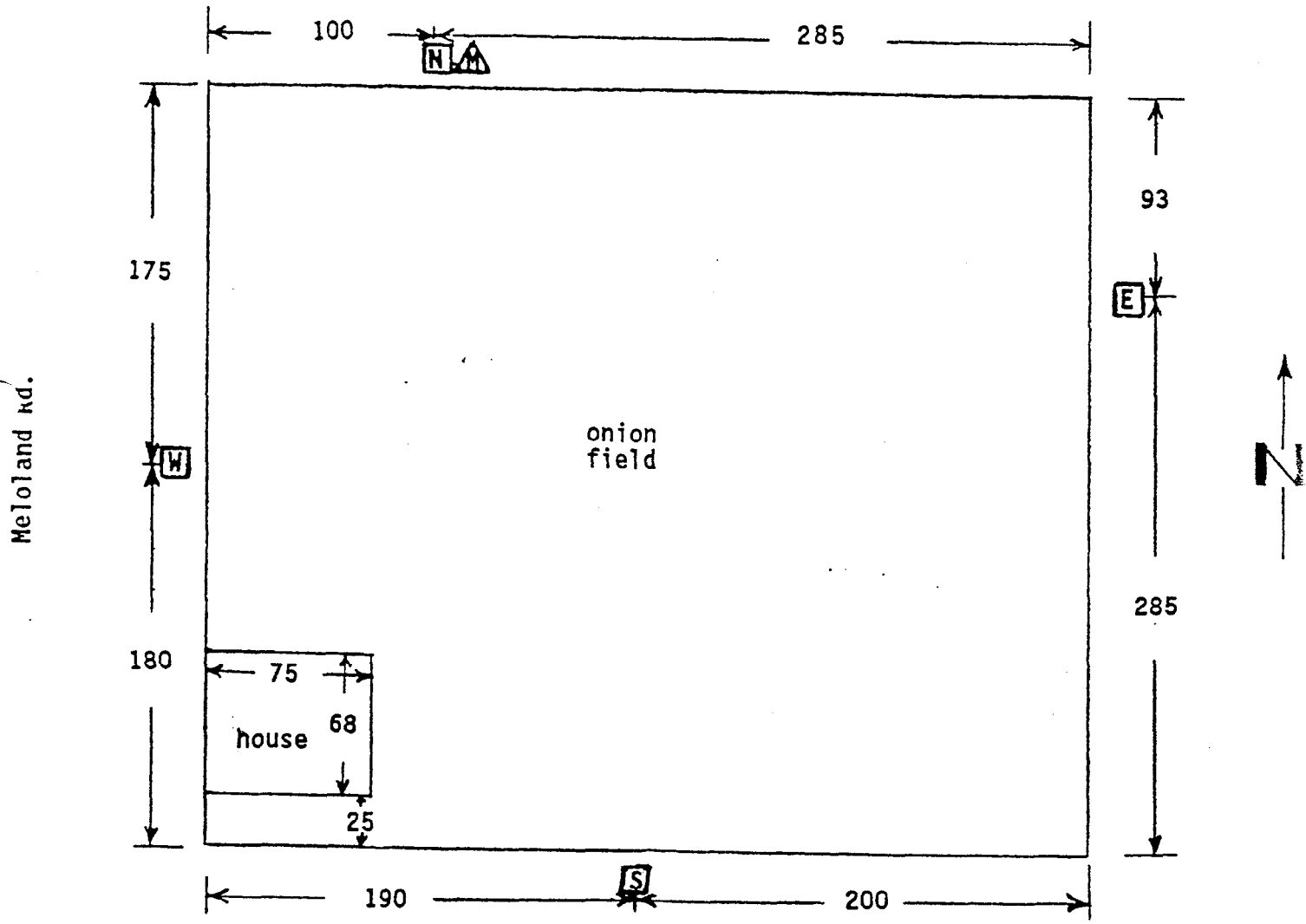


TABLE I. Bromoxynil Application Monitoring Data

Sample ID	Time (min.)	Volume* (m^3)	Total (ug)	Concentration (ug/m^3)	Collection Time (Approx.)
0N	160	0.29	ND	--	Background
0E	160	0.29	ND	--	
0S-1	160	0.29	ND	--	1/19/95
0S-2	160	0.29			
0W	165	0.30	ND	--	(1100-1400)
1N	205	0.37	ND	--	(Application)
1E	205	0.37	ND	--	
1S-1	205	0.37	ND	--	
1S-2	205	0.37	ND	--	
1W	205	0.37	ND	--	1/19/95
1B	---	----		--	(1400-1730)
2N	195	0.35	ND	--	
2E	200	0.36	ND	--	
2S-1	195	0.35	ND	--	
2S-2	195	0.35	ND	--	
2W	195	0.35	ND	--	(1730-2000)
3N	220	0.40	ND	--	
3E	215	0.39	ND	--	
3S-1	220	0.40	ND	--	
3S-2	220	0.40	ND	--	
3W	220	0.40	ND	--	(2000-2330)

*All flows at 1.8 liters per minute (see SAMPLING METHODOLOGY).

ND = Not Detected, <0.04 ug/sample.

No values corrected for percentage of recovery.

TABLE I. Bromoxynil Application Monitoring Data (cont.)

Sample ID	Time (min.)	Volume* (m^3)	Total (ug)	Concentration (ug/m^3)	Collection Time (Approx.)
4N	475	0.86	ND	--	
4E	480	0.86	ND	--	
4S-1	480	0.86	ND	--	
4S-2	480	0.86	ND	--	1/19-20/95
4W	480	0.86	ND	--	(2330-0730)
5N	420	0.76	ND	--	
5E	415	0.75	ND	--	
5S-1	410	0.74	ND	--	
5S-2	410	0.74	ND	--	1/20/95
5W	410	0.74	ND	--	(0730-1400)
6N	330	0.59	ND	--	
6E	330	0.59	ND	--	
6S-1	335	0.60	ND	--	
6S-2	335	0.60	ND	--	1/20/95
6W	335	0.60	ND	--	(1400-2000)
7N	1125	2.0	ND	--	
7E	1120	2.0	ND	--	
7S-1	1120	2.0	ND	--	
7S-2	1120	2.0	ND	--	1/20-21/95
7W	1120	2.0	ND	--	(2000-1430)
8N	1400	2.5	ND	--	
8E	1405	2.5	ND	--	
8S-1	1400	2.5	ND	--	
8S-2	1400	2.5	ND	--	1/21-22/95
8W	1400	2.5	ND	--	(1430-1400)

*All flows at 1.8 liters per minute (see SAMPLING METHODOLOGY).

ND = Not Detected, <0.04 ug/sample.

No values corrected for percentage of recovery.

TABLE II. Bromoxynil Meteorological Data

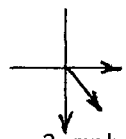
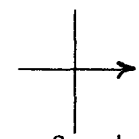
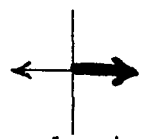
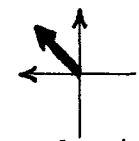
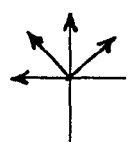
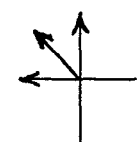
Sampling Period	Wind* Direction	Wind Speed (mph)	Cloud Cover
0	N/NW/W	3	PC/O
1	W	2	PC/O
2	**W**/N/E	1	PC
3	**SE**/E/S	1	PC
4	E/SE/S/SW	2	PC
5	E/SE/S	3	PC/K
6	**SE**/N/NW/S	2	K/PC
7	**E**/NW/N	4	K/PC (light rain)
8	N/S/E/W	2	K/PC/O

BOLD indicates predominant wind direction, if any.

*Indicates direction wind blows from.

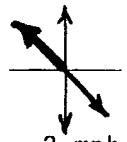
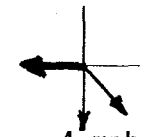
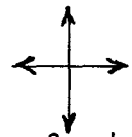
K = clear, PC = partly cloudy, O = overcast

TABLE III. Summary of Bromoxynil Application Data (ug/m^3)

[N] ND (0) [W] ND  [E] ND 3 mph [S] ND	[N] ND (1) [W] ND  [E] ND 2 mph [S] ND
[N] ND (2) [W] ND  [E] ND 1 mph [S] ND	[N] ND (3) [W] ND  [E] ND 1 mph [S] ND
[N] ND (4) [W] ND  [E] ND 2 mph [S] ND	[N] ND (5) [W] ND  [E] ND 3 mph [S] ND

( ) Indicates sampling period. [ ] Indicates sampling site represented. Arrow indicates direction wind is blowing toward. **Bold** indicates predominant wind direction, if any.
ND = not detected, less than the limit of quantitation, 0.04 ug/sample.

TABLE III. Summary of Bromoxynil Application Data (ug/m^3)

(6) [N] ND [W] ND  [E] ND 2 mph [S] ND	(7) [N] ND [W] ND  [E] ND 4 mph [S] ND
(8) [N] ND [W] ND  [E] ND 2 mph [S] ND	

( ) Indicates sampling period. [ ] Indicates sampling site represented. Arrow indicates direction wind is blowing toward. **Bold** indicates predominant wind direction, if any.
ND = not detected, less than the limit of quantitation, 0.04 ug/sample.

TABLE IV. Laboratory Quality Control Data

Bromoxynil Trip Spikes and Blanks

ID	Amount Spiked	Amount Recovered	Percent Recovered
SP-1	0.575 ug	0.500 ug	87
SP-2	1.72 ug	1.80 ug	105
SP-3	2.88 ug	2.79 ug	97
SP-4	0.0 ug	ND ug	--

In-House Laboratory Spikes

ID	Amount Spiked (ug)	Amount Recovered (ug)	Percent Recovered
1	0.23	0.22	96
2	0.23	0.22	96
3	0.23	0.22	100
4	0.567	0.513	89
5	0.567	0.513	89
6	0.567	0.558	97
7	1.15	1.03	90
8	1.15	1.06	92
9	1.15	1.08	94

ND = Not detected, <0.04 ug/sample.

QMOSB Audit Spikes (First Set)

ID	Amount Spiked (ug)	Amount Recovered (ug)	Percent Difference
BRX-1	0.50	0.249	-50.2
BRX-2	0.00	<0.02	0.0
BRX-3	1.00	0.507	-49.3
BRX-4	0.50	0.211	-57.8
BRX-5	0.25	0.048	-80.8
BRX-6	1.00	0.421	-57.9
BRX-7	0.25	0.112	-55.2

QMOSB Audit Spikes (Second Set)

ID	Amount Spiked (ug)	Amount Recovered (ug)	Percent Difference
BRX-8	0.375	0.381	1.6
BRX-9	0.125	0.165	32.0
BRX-10	0.750	0.702	-6.4
BRX-11	0.125	0.165	32.0
BRX-12	0.375	0.381	1.6